

OST TECHNICAL PROGRESS REPORT FOR FY2001

TITLE: CO₂ Capture/Separation Team

TEAM MEMBERS: H. W. Pennline (Team Leader); J. S. Hoffman; M. L. Gray; R. V. Siriwardane; E. J. Granite; M. S. Hilterman; J. T. Yeh; K. J. Champagne; Y. Soong; E. P. Fisher; M. S. Shen

DESCRIPTION: Capture and separation of carbon dioxide (CO₂) from large point sources is a key step in the overall CO₂ sequestration process. It is estimated that the capture step may require a substantial amount of the energy in an overall sequestration scenario. From the draft Carbon Sequestration Program Plan of April 2000 [1], the capture and separation pathway program element targets novel, low-cost approaches to remove carbon or CO₂ from energy production and conversion systems. The time frames to accomplish specific technical milestones for various capture technologies may differ considerably, since some represent opportunities that are adaptations of existing industrial practices, and others are in the early stages of development. The goal of the CO₂ capture and separation area is to isolate carbon from its many sources in a form suitable for transport. The most likely capture and separation technology options, as stated in the report titled Carbon Sequestration Research and Development [2], are chemical and physical absorption; physical and chemical adsorption; low-temperature distillation; and gas-separation membranes.

Within the Carbon Sequestration Program of the Department of Energy, an in-house focus area at the National Energy Technology Laboratory has initiated research projects in this fledgling area. As related to power generation, capture and separation processes can be viewed as near-term and far-term, with the former dealing with conventional fossil fuel combustion, such as pulverized-coal combustion, and with the latter pertaining to advanced power systems, such as advanced integrated gasification combined cycle. For the near-term capture processes, an evolutionary research project had addressed improvements in conventional amine scrubbing to remove carbon dioxide from flue gas. Additionally, other chemical absorption (wet scrubbing) techniques have been proposed to remove a gamut of pollutants from flue gas. In the far-term research effort, novel techniques are being developed to remove carbon dioxide from the fuel gas (synthesis gas) or flue gas from advanced power/energy conversion systems. Chemical absorption, physical adsorption, or electrochemistry are fundamental methods used in the separation step. Most of the processes are regenerable. In two different projects, a sorbent is used where the active component chemically bonds with the carbon dioxide and is later regenerated by using heat or a reducing agent. In another project, the carbon dioxide is adsorbed by the sorbent, and a temperature or pressure swing is performed to remove the carbon dioxide. Another investigation uses an electrochemical cell to separate the carbon dioxide.

RESEARCH OBJECTIVES: The capture and separation task of the in-house portion of the Carbon Sequestration Program conducts in-house research and develops techniques to capture CO₂ from large, stationary point sources. The effort pursues development of control technologies that will be applicable to flue gases from conventional power plants and with other gases, such as fuel/synthesis gas, from advanced power systems. Evolutionary improvements in existing

conventional CO₂ scrubbing technologies can be investigated. However, new concepts for advanced control of CO₂ are emphasized. These concepts will be tested, and experimental studies to provide additional fundamental data and to develop engineering information will be conducted. Projects may range from laboratory-scale work to testing at a scale equivalent to about 0.75 megawatts of electric power.

RELATIONSHIP OF NETL'S PRODUCT LINES: The CO₂ Capture/Separation Team was formed during FY2001. However, the projects that initiated the team's work in FY2000 emanated from the Gasification Product Line and the Environmental Product Line. In FY2001, the projects were restructured within a new team and were primarily funded from the new Carbon Sequestration Product Line.

Specifically, for the in-house research and development effort that is conducted within the capture and separation element of the Carbon Sequestration Program, all of the studies are encompassed within the first two technology categories, as identified in the Carbon Sequestration Research and Development report [2]. In the chemical and physical absorption category, two studies are being conducted. In the first, *CO₂ Scrubbing With Regenerable Sorbents*, nominal conditions for absorption and regeneration chemistry will be identified for alkali- or alkaline earth-based sorbents used in dry scrubbing applications for CO₂ capture. Synthesis gas conditions that mimic those found in a Vision 21 setting [3], particularly at high temperature, will be used for the sorbents. In the second investigation, *Novel Amine-Enriched Absorbents for CO₂ Capture*, the ability to remove CO₂ by incorporating an amine function within a solid support is being explored. Initial screening will develop a database and establish whether this unique dry scrubbing technique is feasible.

In the physical and chemical adsorption category, a study, *Sorbent Development for Carbon Dioxide Separation and Removal: Pressure and/or Temperature Swing Adsorption*, is being performed where various sorbent materials, such as activated carbons and natural or synthesized zeolites, are assessed for their capacity to adsorb/desorb CO₂. An exploratory project, *Electrochemical Devices for Separating and Detecting Carbon Dioxide From Flue Gas*, uses a combination of adsorption and electrochemical-driven transport of CO₂ across a membrane to remove CO₂ from gas mixtures. Carbonate-ion conducting solid electrolytes and electrodes are the materials of choice for this novel concept.

SUMMARY ACCOMPLISHMENTS:

***Presentations at First National Carbon Sequestration Conference**

Three researchers from the team presented their manuscripts at the First National Carbon Sequestration Conference held in Washington, DC during May 2001. Dr. Ranjani Siriwardane presented her most recent results from her pressure swing adsorption studies. Dr. James Hoffman discussed his findings with low- and high-temperature sorbents for carbon dioxide removal from flue or fuel gases. Mr. McMahan Gray informed the research body of his results with adhering amines to substrates that are then used to remove carbon dioxide from gas streams. The manuscripts were well-received as determined by the number of foreign and domestic inquiries with respect to the work.

***Dry, Regenerable Sorbent Investigation for CO₂ Capture**

An experimental study was performed to evaluate the potential of alkali metals for use as dry, regenerable sorbents for the capture of CO₂ from a gas stream. Thermodynamic analysis that identified ranges of temperature for absorption and regeneration to be thermodynamically feasible directed that potassium carbonate would be the first candidate to be investigated. An application for this sorbent could be downstream of the economizer in a coal-fired power plant at a low absorption temperature (less than 145 °C). Experiments were conducted in both a thermogravimetric analysis (TGA) reactor and in a packed-bed reactor using sorbent fabricated from potassium carbonate supported on a high surface area, activated alumina. Results indicated that CO₂ capture is favored at low absorption temperatures (50-60 °C), with thermal regeneration easily occurring at 150 °C. The information obtained in the testing was reduced to determine the feasibility of the cyclic process with potassium carbonate at a larger scale. Additionally, other sorbents that can withstand the harsh environment of IGCC conditions are being investigated.

***Improved Sorbents May Optimize Pressure Swing Adsorption (PSA) / Temperature Swing Adsorption (TSA) Process**

Synthetic zeolites from Sud Chemie showed excellent CO₂ adsorption capacities (7-8 moles of CO₂/kg of sorbent) and preferential adsorption of CO₂ from gas mixtures at high pressures. These sorbents can be regenerated by either lowering the pressure or increasing the temperature. Since these sorbents showed significantly higher CO₂ adsorption capacities than that obtained with commercial technologies, these could potentially be used in PSA/TSA systems to remove CO₂ from high pressure gas streams, such as those found in IGCC applications. In addition, a new type of CO₂ removal sorbent was also developed with excellent regenerability. A consistent CO₂ removal performance was observed during multi-cycle tests with this new sorbent.

***Key Fabrication Steps Improve CO₂ Capture**

The capture of CO₂ from gas streams has been achieved by the utilization of amine-enriched, solid-sorbent systems. The initial solid sorbents were generated by the chemical treatment of carbon-enriched fly ash concentrates with various amine compounds. It was determined that these amine-enriched fly ash carbon concentrates performed at an 18% CO₂ capture capacity based on commercially available sorbents. Alternative oxygen rich solids, such as silica gel, activated carbon, and molecular sieves, were prepared and examined as potential sorbents for the capture of CO₂ from gas streams. The improved chemical sorption performance of these new solid amine sorbents will be described in future reports.

RESULTS:

In the investigation *CO₂ Scrubbing With Regenerable Sorbents*, a unique approach for CO₂ capture employs dry scrubbing -- a process that includes chemical absorption with a sorbent. A dry, regenerable sorbent process has been proposed that is cyclic in the sense that the sorbent can remove the pollutant and subsequently be regenerated (and in this step yields a concentrated stream of CO₂). The process can be economically advantageous over commercially available wet

scrubbing technologies. Although the process can be used in flue gas separations, it can also be used to capture CO₂ from gasification streams at high temperatures. Depending on the level of CO₂ abatement necessitated in the future due to international treaties or national regulations, CO₂ allowances, similar to current SO₂ credits, could be available to electric utilities for achieving partial CO₂ reduction. The proposed process will be capable of either near-total or partial removal of CO₂ from the point source.

With respect to an IGCC process, the CO₂ absorption reactor could be integrated into one of several IGCC process locations. The site of integration would depend on the nominal operating parameters (i.e., temperature, etc.) required for the particular sorbent of interest. For instance, the alkali metal carbonates/bicarbonates ("low temperature") are more suitable for placement near the downstream end of the stack gas process line. The alkaline-earth oxides/carbonates ("high temperature") are potentially more adaptable for use in gasification where the absorber would be located upstream of the gas turbine. The synthesis gas location represents a highly-reducing atmosphere, whereas the stack gas location represents a more traditional flue gas location containing oxygen. These substantial differences in gas atmospheres need to be considered when integrating a CO₂ capture process into the IGCC system. However, depending on the sorbent, thermodynamic calculations [4] indicate that the dry, regenerable process can be situated at more than one location within the IGCC process.

The objective is to identify regenerable sorbents that could be used for the capture of CO₂ from a gas stream and to validate the dry, regenerable sorbent process that is capable of removing CO₂ from a gaseous stream. The experimental approach taken in this research effort is to utilize a TGA to track sorbent weight change as the material is exposed to gases under conditions representative of absorption or regeneration. Change in sorbent weight can be linked to the extent of chemical reaction, from which kinetic information can be extracted. Additionally, scaled-up experiments will be performed in a packed-bed reactor to complement the TGA study.

Findings [5] with a supported potassium bicarbonate sorbent revealed that carbon dioxide would react with the sorbent to form the carbonate and that the sorbent was regenerable, but the kinetics of the reaction were slow. Calcium oxide was adopted as the prime candidate. The thermodynamic analysis of carbonation of calcium oxide indicates that the reaction has potential application for systems at relatively high temperature. Based on the calculated equilibrium constants, the forward and reverse reaction rate constants become equal at approximately 860 °C. Hence the CO₂ absorption (forward) reaction appears more favorable between 750-860 °C, while thermal regeneration (decomposition or the reverse reaction) is attainable at temperatures higher than 860 °C (near 1000 °C).

The CaO reagent TGA study [5] revealed ranges of temperature suitable for absorption and regeneration reactions to occur and confirmed the thermodynamic results. The CO₂ absorption reaction appears most favorable between 750-850 °C, while regeneration (decomposition or the reverse reaction) is attainable at 1000 °C. The absorption reaction is initially very fast (perhaps 50% conversion after an hour), followed by a much slower rate, due most likely to diffusional limitations from formation of a product layer of CaCO₃. By raising the temperature from 850 °C to 1000 °C, the sample can be rapidly regenerated within approximately fifteen minutes.

Additional testing will incorporate a support for the calcium oxide and will investigate other promising sorbents.

In the study *Novel Amine-Enriched Sorbents for CO₂ Capture*, the objective is to develop amine-enriched sorbents for the capture of CO₂ from flue gas streams generated by the utility industry. One commercial approach to capture CO₂ from flue gases is the process based on the principle of chemical absorption of CO₂. Wet chemical stripping of CO₂ involves one or more reversible chemical reactions between CO₂ and a solvent, such as an amine, to produce a liquid species which, upon heating, decomposes to liberate CO₂ and regenerate the original solvent. Examples of solvents (or absorbents) in commercial application are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA).

However, capture of CO₂ from flue gas produced from coal combustion using an MEA scrubbing system will involve a large energy penalty [6], and the absorption step is influenced by the availability of gas/liquid interaction surfaces and the concentration of the amine in the aqueous solution [7]. The regenerative step of the amine process is, in general, energy intensive. The high energy requirement of these processes is related partly to their low capacity (CO₂ absorbed per unit mass) and high water fraction, such that a large body of liquid must be heated upon regeneration to release a small amount of gas.

Energy savings can be achieved if a solvent/sorbent that has high absorption capacity at moderate temperatures and pressures can be developed. The higher the absorption capacity, the less quantity of solvent required to handle a given gas stream and the less sensible and latent energy is required in the regeneration step. Therefore, new novel solvents/sorbents to reduce total capital and operating costs need to be developed.

Novel CO₂ capture sorbents are being prepared by the chemical treatment of high surface oxide materials (e.g., activated carbon with density of 2.3 g/cm³ has a surface area of 400 m²/g with a contact area of 919,000,000 m²/m³) with various amine compounds. The implanting of amine groups on the high surface area material increases the contact area between CO₂ and amine by several orders of magnitude. Furthermore, the mass and heat-transfer problems are reduced significantly due to the novel concept of gas-amine-enriched solid reactions for CO₂ capture versus that of gas-liquid reactions. Therefore, only a small amount of sorbent is needed for capturing the same amount of CO₂ compared to that for the typical amine processes. Thus, a significant improvement in the efficiency of the process is accomplished due to the increased contact area and decreased energy consumption for regenerating the absorbents. In addition, the high surface area material could provide the physical/chemical adsorption function for CO₂, similar to PSA or TSA, which will enhance the CO₂ capture process.

High-surface area oxide surface materials were modified with amine groups, and the CO₂ capture capacity of these modified samples was studied with pure CO₂ and simulated flue gas mixtures. In addition, exploratory work with a TPD/DRIFT study of amine enriched sorbents for the capture of CO₂ is being conducted [8,9]. A variety of solid materials, including flyash derivatives, activated carbon, and silica gel, were enriched with amine and tested as sorbents for capture of CO₂. Absorption occurred in the presence of moisture at temperatures of 25–30 °C, and the TPD

study for CO₂ desorption was conducted over the temperature range of 30–120 °C. Results indicated that this amine treatment can be successfully applied to a variety of solid substrates with excellent absorptivity and regeneration. The CO₂ capture capacities were improved for all of the solid substrates, and the amine-treated sorbents have demonstrated the ability to capture CO₂ from gas streams in a moist environment. It is also important to note that current CO₂ capture experimental procedures are based only on the chemisorbed species; physisorbed CO₂ is purged from the surface prior to the desorption stage. Consequently, additional work is required to refine the experimental procedures to include the physisorbed CO₂ and thus increase measured capture capacities. In addition, the possible deactivation and oxidation of the amine-enriched sorbents in flue gas mixtures will be studied.

In the investigation entitled *Sorbent Development for Carbon Dioxide Separation and Removal -- Pressure Swing Adsorption and Temperature Swing Adsorption*, either PSA or TSA is identified as a viable method to remove CO₂ from high pressure gas streams, such as those encountered in IGCC systems. PSA processes are based on preferential adsorption of the desired gas (for example, CO₂) on porous materials at a high pressure. When the pressure is decreased, the gas is desorbed from the porous sorbent, and the sorbent can be reused for subsequent adsorption. Two large scale PSA processes for separation of CO₂ were developed by Japanese firms [10]. Molecular sieves and activated carbons have been the preferred sorbents for the process. It is also reported that higher energy penalties are associated with the utilization of molecular sieves than with the amine process [11]. However, during the last decade several new PSA process concepts have been reported in the literature to improve the performance. While it is important to consider the improved process design of the PSA systems to enhance the recovery rate, it is equally important to utilize sorbents with high CO₂ adsorption capacity, high selectivity for CO₂, high diffusivity, high rates of adsorption, and high regenerability.

Recovery rates can also be enhanced if PSA systems are utilized in high pressure gas streams, since some PSA sorbents have shown superior adsorption capacity at higher pressures. According to an IEA coal research report [12], the PSA/TSA processes may be more suitable for CO₂ capture from gasification processes. It should be possible to make the PSA/TSA technique superior to the existing CO₂ capture techniques by utilizing proper system designs and sorbents with high capacity.

One objective of this study is to develop regenerable sorbents that have high selectivity, high regenerability, and high adsorption capacity for CO₂. These properties are critical for the success of the PSA/TSA process. Past findings [13,14] indicate that molecular sieves, natural and synthetic zeolites, and activated carbons preferentially adsorb carbon dioxide in volumetric adsorption/desorption isotherms from simulated fuel gas mixtures. Similarly, high pressure microreactor studies were conducted to understand the competitive adsorption of CO₂ from a gas mixture containing 15% CO₂, 82% N₂, and 3% O₂ saturated with water vapor at ambient temperature. Excellent separation of CO₂ from gas mixtures was observed for the sorbents mentioned above, and the presence of water vapor does not seem to affect the sorbent performance. Sorbent capacities were equal to or better than those obtained from CO₂ commercial processes. The sorbent tests conducted have also shown that the amount of CO₂ adsorbed on some synthetic and natural zeolites can be increased substantially by increasing the

pressure from 1 atm to 20 atm. Future work will continue to investigate sorbents for CO₂ capture and attempt to determine the adsorption mechanism. Additionally, the PSA/TSA systems would be even more energy efficient if the sorbents are operational at moderate or high temperatures [12], and thus development of high/moderate temperature sorbents for PSA/TSA processes will be investigated.

A novel exploration, *Electrochemical Devices For Separating and Detecting Carbon Dioxide*, seeks to develop cost effective electrochemical devices for the separation of carbon dioxide. These electrochemical pumps are efficient, silent, and non-polluting and are a far simpler and potentially more cost-effective means of carbon dioxide separation utilizing a carbonate ion-conducting membrane. The electrochemical pumps will initially be based upon the readily available molten carbonate and lithium carbonate solid electrolytes. A goal is the development of improved carbonate-ion conducting solid electrolytes, allowing for even better electrochemical pumps.

The application of an external EMF (voltage) to a carbonate ion-conducting solid electrolyte through a closed circuit will cause carbon dioxide to be selectively transported (pumped) to/or from a metal electrode. The rate of carbon dioxide transport is given by the current (flux of carbonate ions) across the membrane. Several factors limit the transport of carbon dioxide across the membrane. These are: 1) the conductivity of the electrolyte, 2) the thermodynamic stability of the electrolyte, and 3) the electrode kinetics. Additionally, the power consumption is related to the resistance of the pump. The overall resistance of the pump is the sum of the resistances due to both electrodes, the electrolyte, and the electrode and electrolyte contacts.

Overall resistance can be minimized by: 1) use of a thin electrolyte and electrodes, 2) having intimate contact between electrode and electrolyte, and 3) selecting an electrolyte with high conductivity. For a laboratory-scale separator that is currently being constructed, with an applied voltage of around one volt and a resulting current in the milliamp range, the power requirements will be on the order of milliwatts. Electrolytes with higher conductivity than the baseline lithium carbonate electrolyte will be developed in order to reduce the device size and power required for carbon dioxide separation.

To date, a reactor system to accommodate the testing has been designed and assembled. Various novel solid electrolyte disks for electrochemical pumps have been prepared and characterized via inductively coupled plasma-atomic emission spectra and x-ray diffraction studies. Future tests will optimize the transport of carbon dioxide from simulated flue gas mixtures across the electrolyte.

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Comments or questions pertaining to the individual projects can be addressed to the project leader:

CO₂ Scrubbing with Regenerable Sorbents.....James Hoffman

Novel Amine-Enriched Absorbents for CO₂ Capture..... McMahan Gray

Sorbent Development for Carbon Dioxide Separation and Removal -- Pressure Swing Adsorption and Temperature Swing

Adsorption.....Ranjani Siriwardane

Electrochemical Devices for Separating Carbon Dioxide from Flue Gas.....Evan Granite